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54 **Process for preparing sucrose fatty acid ester powder.**

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**Reverse Osmosis, S. Sourirajan, Logos
Press, London 1970**

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Description

The present invention relates to an industrially useful process for preparing sucrose fatty acid esters. More particularly, the present invention relates to a process for preparing sucrose fatty acid esters in an aqueous system through the whole steps, including reaction step of sucrose and fatty acid alkyl esters and purification step for the product, without using an organic solvent, wherein the unreacted sucrose can be recovered in high yield.

Sucrose fatty acid esters (sugar esters) useful as surface active agents are prepared industrially at present by either a solvent process wherein sucrose is reacted with a methyl ester of a higher fatty acid having 8 to 22 carbon atoms in the presence of a suitable catalyst in an organic solvent such as dimethylformamide or dimethylsulfoxide, as disclosed in Japanese Patent Publication Kokoku No. 35-13102; or an aqueous medium process wherein sucrose is formed into a molten mixture with a fatty acid salt (soap) using water without using an organic solvent, and is then reacted with a higher fatty acid methyl ester in the presence of a catalyst, as disclosed in Japanese Patent Publication Kokoku No. 51-14485.

However, even according to any of these processes, the obtained reaction mixture contains impurities such as the unreacted sucrose, the unreacted fatty acid methyl ester, residual catalyst, soap, free fatty acid and the like in addition to the desired sucrose fatty acid ester. These impurities, at least impurities whose contents exceed the specified amounts must be removed prior to being put on the market. Particularly, in case of sucrose fatty acid esters used as a food additive which requires a high purity, removal of high boiling polar solvents such as DMF remaining in the product produced by the solvent process is very important in view of recent strict legal regulation, but it requires complicated procedures. The aqueous medium process has no problem of contamination of the product with the reaction solvent, but it still requires the purification treatment since large amounts of impurities are included in the reaction mixture.

In general, the conversion of sucrose is low. For example, in case of the process using dimethylformamide as the reaction medium, the conversion is at most 50 %. Accordingly, recovery of the unreacted sucrose is also important.

In order to remove the impurities and to recover the unreacted sucrose from the reaction mixture (namely crude sucrose fatty acid esters), various processes for the purification of crude product have hitherto been proposed. These purification processes usually require a large amount of organic solvents, e.g. butanol, toluene and methyl ethyl ketone. However, in the production of sucrose fatty acid esters on an industrial scale, the use of a large amount of organic solvents has the following disadvantages: (1) risk of explosion and fire, (2) provision of explosion and fire prevention means to electric devices, (3) application of closed system to production equipment for explosion and fire prevention, (4) requirement of fireproof construction for entire building by way of precaution against explosion and fire, (5) rise in fixed cost due to the items (2), (3) and (4), (6) rise in materials cost due to loss of solvent, (7) contamination of the product with remaining solvent, and (8) adverse influence on health of workers, and increase of cost resulting from increase in labor required for the prevention therefor.

The disadvantages resulting from the use of organic solvents are an obstacle particularly to the production of sucrose fatty acid esters on an industrial scale. In view of these circumstances, it has been desired to develop a purification technique capable of removing the unreacted sucrose and other impurities from the crude reaction mixture without using organic solvents.

Thus, purification processes using no organic solvent have hitherto been proposed. For example, as representative methods, there have been known (1) a method wherein a sucrose fatty acid ester is precipitated by addition of an acidic aqueous solution to the reaction mixture, as disclosed in British Patent No. 809,815 and (2) a method wherein a sucrose fatty acid ester is precipitated by addition of an aqueous solution of a common neutral salt to the reaction mixture, as disclosed in Japanese Patent Publication Tokyo Kokoku No. 42-8850.

However, these methods have disadvantages. When an acidic aqueous solution, for example, hydrochloric acid, is added to the reaction mixture as in the method (1), the sucrose fatty acid ester immediately deposits, but the unreacted sucrose is easily decomposed and converted into glucose and fruit sugar. This cannot be avoided even if the addition is conducted at a low temperature (e.g. 0° to 5°C). Accordingly, the recovery and reuse of the unreacted sucrose are difficult.

The addition of an aqueous solution of a neutral salt such as sodium chloride or Glauber's salt, as in the method (2), causes sucrose fatty acid esters to deposit rapidly. In this case, decomposition of unreacted sucrose does not occur, but the monoester which is an effective component in the product is dissolved in an aqueous phase. Consequently, not only the dissolution results in a large loss of the product, but also it is a hindrance particularly to production of sucrose fatty acid esters having a high HLB which are recently in great demand. Usually, the sucrose esters have an HLB value of 1 to 20, and the larger the HLB value, the

higher the hydrophilic property.

In order to industrially realize the purification of crude sucrose fatty acid esters using water, it is also important to give consideration to recovery of the unreacted sucrose, and drying of wet product incident to the use of water as a purification solvent.

Since the purification of the reaction mixture with the use of water is based on difference in water solubility between a sucrose fatty acid ester and unreacted sucrose, migration of a large amount of unreacted sucrose into an aqueous phase cannot be avoided. The manufacture of sucrose fatty acid esters cannot be industrially accepted unless such a dissolved sucrose is recovered. Accordingly, it is very important to efficiently recover the sucrose which has transferred into an aqueous phase upon purification.

The water-containing sucrose fatty acid ester which has been separated from the reaction mixture and to be dried, is usually in the form of an aqueous solution when the water content is over 80 % by weight, and is in the form of a slurry when the water content is less than 80 % by weight. In general, an aqueous solution of a sucrose fatty acid ester shows a peculiar viscosity behavior such that the viscosity rapidly increases from about 40°C, reaches maximum at about 50°C and rapidly drops over 50°C. Some problems are encountered in removing water from the sucrose fatty acid ester in the form of an aqueous solution or slurry. The evaporation of water by heating under vacuum, for example, using a usual agitated vacuum dryer, is practically difficult because of marked foaming. In particular, due to the property of sucrose fatty acid ester that the softening point or melting point is low (for example, sucrose monostearate having a melting point of about 52°C, and sucrose distearate having a melting point of about 110°C), the sucrose fatty acid ester itself tends to be hydrated at the final stage of evaporation of water. This makes the dehydration more difficult. Moreover, when the evaporation is conducted at a high temperature and the contacting time with a heating source is long, not only the sucrose fatty acid ester is decomposed, resulting in marked coloration or caramel formation, but also the acid value is raised by free fatty acid formed by decomposition, as disclosed in Japanese Patent Publication Tokkyo Kokoku No. 37-9966. In addition, it is also a cause which makes the drying difficult that the latent heat of evaporation of water is very high (more than 500 kcal/kg H₂O) and the evaporation temperature is high.

Other usual drying methods are also not suitable for preparing dry sucrose fatty acid esters. For example, in case of using a flash dryer wherein a slurry is continuously heated, fed to a vacuum chamber and released thereto, various difficulties are encountered when a sufficient drying is desired because of a large latent heat of water. Even if these difficulties are overcome, the sucrose ester dehydrated and dried under vacuum is in the molten state and, therefore, it requires a pulverization step after taking out of the drier and cooling to less than the melting point to solidify, for instance, by blowing a cold air. In addition to many steps being required, there is a risk of dust explosion in the final pulverization step.

Accordingly, it is also important to solve the problems encountered by drying in realizing the purification of sucrose fatty acid esters using water as the purification solvent.

The document DE-A-3 047 122 relates to an improvement of the separating action in ultrafiltration of aqueous cleaning solutions containing oils, fats and surfactants by addition of unsaturated fatty acids or water-soluble salts thereof to the cleaning solutions, thereby raising the retention of oils, fats and surfactants in the retentate.

The document REVERSE OSMOSIS, S. Sourirajan, Logos Press Ltd., London, 1970 p. 245-255 discloses the application of reverse osmosis to aqueous sucrose solutions.

It is a primary object of the present invention to provide a process for preparing a purified sucrose fatty acid ester without using organic solvents in both the reaction step and the purification step, which is suitable for the production of the sucrose ester on an industrial scale.

A further object of the invention is to provide a process for recovering a sucrose fatty acid ester free from organic solvents from the crude reaction mixture, with recovery of unreacted sucrose in high yield.

A still further object of the invention is to provide an industrially useful process for purifying a sucrose fatty acid ester using water as the purification solvent without substantial loss of the sucrose fatty acid ester and sucrose.

Another object of the invention is to provide a process for preparing a dry powder of a highly pure sucrose fatty acid ester having a high HLB with ease and without deteriorating the quality in the drying step, while recovering the unreacted sucrose.

Still another object of the invention is to provide a process for preparing a dry powder of a highly pure sucrose fatty acid ester having a low HLB with ease and without deteriorating the quality in the drying step.

These and other objects of the present invention will become apparent from the description hereinafter.

The present inventors have made experiments about salting out in the purification of crude product using water as the purification medium in order to achieve the following purposes: namely (1) minimizing the amount of sucrose fatty acid esters dissolved in an aqueous phase, (2) preventing decomposition of

unreacted sucrose, (3) purifying the precipitated sucrose fatty acid esters and forming a dry powder thereof, and (4) efficiently recovering the unreacted sucrose from the filtrate (or supernatant) obtained by removing the above-mentioned precipitate.

It has been found that when a neutral salt is dissolved in an aqueous solution of the reaction mixture obtained by the reaction of sucrose and a fatty acid alkyl ester in an aqueous system, a large portion of the sucrose fatty acid esters is precipitated under a proper combination of pH, temperature, concentration of neutral salt and amount of water, and moreover, a salt derived from the reaction catalyst is included in the aqueous phase with the unreacted sucrose. Thus, on the basis of this discovery, it has now been found that the unreacted sucrose and the catalyst-derived salt can be separated from the sucrose fatty acid esters, without substantial loss of sucrose fatty acid esters, by repeating the salting out procedure, namely by dissolving the precipitated sucrose fatty acid esters again in water and repeating the precipitation procedure by the addition of an aqueous solution of the neutral salt, and that the unreacted sucrose can be efficiently recovered from the residual liquid after removal of the above precipitate by contacting it with an adequate reverse osmosis membrane.

It has been further found that sucrose fatty acid esters having a high HLB included in the precipitate is transferred into an aqueous phase by washing the precipitate with an acidic water having an appropriate pH, while leaving sucrose fatty acid esters having a low HLB as the solid, and that the recovery of sucrose fatty acid esters having a high HLB transferred into the aqueous phase, which has not been achieved by conventional processes, can be made on an industrial scale by means of ultrafiltration to give an aqueous solution of purified sucrose esters and from which a powder can be obtained without deterioration of the quality by spray drying, while the sucrose fatty acid esters having a low HLB can be obtained in the form of a dry powder from the solid remaining after the washing treatment with an acidic water by spray drying the solid in the form of a slurry.

According to the invention there is provided a process for preparing a powder of sucrose fatty acid esters, which comprises

- a. reacting sucrose with a fatty acid alkyl ester in an aqueous reaction system containing a catalyst to produce a sucrose fatty acid ester,
- b. adjusting the resulting reaction mixture to a neutral pH region,
- c. adding water and a neutral salt to the reaction mixture to precipitate the sucrose fatty acid ester product containing sucrose fatty acid and esters having high and low HLB,
- d. separating the resulting precipitate from the liquid phase,
- e. extracting the high HLB fraction by washing the precipitate with an acidic water,
- f. subjecting the resulting washing liquid to ultrafiltration,
- g. spray drying the resulting concentrate in the form of an aqueous solution, and
- h. recovering the unreacted sucrose by subjecting the liquid phase of step d) to reverse osmosis.

Thus, according to the present invention, from the reaction mixture, it is now possible (1) to remove the impurities, (2) to recover unreacted sucrose, (3) to obtain a powder of purified sucrose fatty acid esters having a high HLB and (4) to separate SE product into sucrose fatty acid esters having a high HLB and those having a low HLB, without using organic solvents on an industrial scale.

Fig. 1 is a triangular graph showing the liquid-cake equilibrium relationship between the distribution of sucrose fatty acid esters (having a high HLB) being dissolved in aqueous phase and (having a low HLB) being in the precipitated cake.

(Synthesis of sucrose fatty acid esters by aqueous medium process)

In the present invention, sucrose fatty acid esters (hereinafter referred to as "SE") are prepared from sucrose and a fatty acid alkyl ester by a known aqueous medium process. For example, sucrose is formed into a molten mixture with a fatty acid soap in the presence of water and is reacted with a higher fatty acid alkyl ester such as methyl ester in the presence of a catalyst such as potassium carbonate, as disclosed in Japanese Patent Publication Tokkyo Kokoku No. 51-14485. The production of SE by the aqueous medium process is advantageous in that the reaction mixture does not contain an organic solvent as used in the reaction according to the solvent process, though the reaction mixture contains a larger amount of the soap as compared with the solvent process.

In general, the reaction mixture obtained by the aqueous medium process has approximately the following composition.

Ingredients	% by weight
SE	15 to 74
Unreacted sucrose	1.0 to 80
Unreacted fatty acid methyl ester	0.5 to 10
Salt derived from K_2CO_3	0.05 to 7
Soap	10 to 50
Fatty acid	0.5 to 10

In that case, the proportion of the monoester in the SE is from 10 to 75 % by weight and the proportion of di- and higher esters is from 90 to 25 % by weight.

Also, the acid radical mainly included in each of the fatty acid methyl ester, soap and fatty acid is usually a saturated acid radical having 16 to 22 carbon atoms common to them.

(Addition of water and neutralization)

To the reaction mixture which has the above-mentioned composition, water is added in a water/reaction mixture ratio of 5 : 1 to 40 : 1 by weight, preferably 20 : 1 by weight, while the pH is adjusted to 6.2 to 8.2, preferably 7.5.

When the ratio of water to the reaction mixture is less than 5, the viscosity of the obtained aqueous solution is high and the following procedures become difficult. Also, when water is added in excess to the reaction mixture such that the weight ratio of water to the reaction mixture exceeds 40, the viscosity of the obtained aqueous solution is low and accordingly the following procedures become easy, but a large energy cost is required in removing water upon recovery of unreacted sucrose, etc., thus the economy is impaired.

In order to prevent decomposition of the desired SE, it is preferable to adjust the aqueous solution of the reaction mixture to pH of 6.2 to 8.2. When the pH is more than 8.2, there is a possibility that SE is quantitatively hydrolyzed by an alkali. On the other hand, even in a weak acidic region of less than pH 6.2, there is a fear of acid hydrolysis of SE, for example, when it is exposed to a high temperature over 90 °C.

(Salting out)

A neutral salt is added to the thus pH-adjusted aqueous solution of the reaction mixture, preferably with keeping at a temperature of 50 ° to 80 °C in order to salt out SE rapidly.

Any of neutral salts can be used so long as they are soluble in water and nontoxic. Representative examples of the neutral salt are, for instance, sodium chloride, Glauber's salt ($Na_2SO_4 \cdot 10H_2O$), a lactic acid salt such as potassium lactate and an acetic acid salt such as potassium acetate.

It has been found that when the concentration of the neutral salt is maintained at not less than 5.5 % by weight, preferably not less than 6 % by weight, and when the aqueous solution containing SE precipitate formed by adding the neutral salt is heated to a temperature of 50 ° to 80 °C, the greater part of SE is precipitated regardless of the kinds of neutral salts to be added. This is a peculiar phenomenon and is of important value in connection with the objects of the present invention. By utilizing this phenomenon, SE can be separated in the form of a slurry or cake from the unreacted sucrose, the salt derived from the catalyst and the neutral salt which have transferred to the aqueous phase. Since the aqueous phase is not acidic, sucrose is not decomposed and, therefore, it can be recovered and reused, as occasion demands.

Table 1 shows this phenomenon more clearly. When Y (g) is the weight of SE dissolved in an aqueous phase and X (g) is the weight of SE precipitated, the weight percentage (ϕ %) of SE dissolved in the aqueous phase based on the whole SE (X + Y) is shown by the following equation:

$$\phi = \frac{Y}{X + Y} \times 100 \text{ (\% by weight)}$$

Experiment was made under the following conditions by using a crude SE.

Conditions

Temperature = 75 °C

pH = 7.8

5 Water/crude SE = 20/1 by weight

Fatty acid radical: stearic acid

Composition of crude SE (% by weight)	
SE	94 %
Unreacted fatty acid methyl ester	2 %
Soap	2 %
Fatty acid	1 %
Others	1 %

Composition of SE (% by weight)	
Monoester	73 %
Di- and higher esters	27 %

Table 1

Weight ratio of water/neutral salt added	ϕ (weight % of SE dissolved in water)
99.8/0.2	99.0
98.5/1.5	3.5
97.5/2.5	2.6
95.0/5.0	1.9
94.0/6.0	1.2
92.5/7.5	1.0
90.6/9.4	1.3
87.5/12.5	1.2

By determining the amount of neutral salt to be dissolved in the aqueous solution of the reaction mixture and adding it to the aqueous solution, approximately the whole amount of SE can be precipitated, and by separating the precipitate from the aqueous phase, for example, by means of filtration or centrifugation, neutral salt and sucrose dissolved in the aqueous phase can be easily removed.

(Recover of unreacted sucrose by reverse osmosis)

It is also important to selectively separate and recover unreacted sucrose from the thus treated aqueous solution from which the precipitated SE has been removed, namely the aqueous phase containing unreacted sucrose, a salt derived from catalyst (K_2CO_3) and the neutral salt added for salting out. The present inventors have found that utilization of a reverse osmosis membrane is particularly effective for this purpose. After separating the precipitated SE in a usual manner, for example, by filtration, the filtrate is subjected to reverse osmosis.

It is expected that if a fractionation molecular weight ranging from 130 to 200 is selected as that of the reverse osmosis membrane, the unreacted sucrose (molecular weight: 342) and the SE (molecular weight: more than 600) which has incidentally leaked into the aqueous phase in the prior salting out step, would be filtered off without any problem by the reverse osmosis treatment. On the other hand, substances having a molecular weight less than the fractionation molecular weight of 130 to 200, namely the salt derived from catalyst such as potassium lactate (molecular weight: 128) and the neutral salt added, would pass through fine pores of the reverse osmosis membrane without any problem.

As a result of conducting a large number of experiments on the basis of the above presumption, it has been found that when an aqueous solution containing sucrose, the salt derived from catalyst, the neutral salt

added in the salting out step, and sometimes further a slight amount of SE, is brought into contact with a reverse osmosis membrane having a fractionation molecular weight of about 150 to about 200 at a temperature of 40 ° to 60 ° C under a pressure, the salt derived from catalyst and the neutral salt easily pass with water through fine pores of the membrane. By this reverse osmosis procedure, low molecular weight substances such as the catalyst-derived salt and the neutral salt added for salting out and water are removed from the impure aqueous sucrose solution (which may contain a slight amount of SE) to thereby form the concentrated aqueous solution of crude sucrose. An aqueous sucrose solution having a higher purity can be obtained by dissolving the concentrate in fresh water again and subjecting the solution to the reverse osmosis treatment in the same manner, and if necessary, further repeating these procedures.

The temperature of the aqueous solution to be fed to the reverse osmosis is important for obtaining a good result. If the temperature is lower than 40 ° C, the treating ability is remarkably lowered. Accordingly, it is desirable to select a temperature over 40 ° C from a practical point of view. On the other hand, it is advisable to conduct the treatment at a temperature below 60 ° C, from the viewpoint of the heat resistance of the reverse osmosis. The pH of the aqueous solution to be treated is also important, and the pH ranging from 6.2 to 8.2 is preferred because a fear of influence on the quality of sucrose is minimized.

Recently, various reverse osmosis membranes have been put on the market from various companies. Among them, for instance, reverse osmosis membranes of polyamide, crosslinked polyamide or polyether have excellent properties such as durability, heat resistance, acid resistance, alkali resistance, fungus resistance and pressure resistance. Such membranes are commercially available, for example, under a trade mark "SU-200" from Toray Engineering Kabushiki Kaisha, which has a fractionation molecular weight of about 200 and is suitable to attain the objects of the invention.

In the case of using the reverse osmosis membrane with the fractionation molecular weight of about 200, the treatment of the aqueous solution can be achieved with an industrially acceptable capacity by adjusting the upper limit of the concentration of the solute in the aqueous solution to be supplied to the membrane to about 20 % by weight, preferably about 15 % by weight.

When the solute concentration is more than 20 % by weight, it is difficult to pass water and the salt derived from the catalyst through fine pores of the membrane, and accordingly it is obliged to increase the pressure to be applied as the actuation force for reverse osmosis, thus resulting in increase of the area of the reverse osmosis membrane. This is also very uneconomical because of necessity of great electric power. On the other hand, when the aqueous solution contains the solute in a concentration of about 8-15 % by weight, it is sufficiently possible to industrially isolate sucrose.

For example, when passing an aqueous solution having the composition shown in Table 2 through the reverse osmosis membrane "SU-200" with an effective area of 8 m² per unit at 50 ° C and pH 7.5 and under a pressure applied as the actuation force for reverse osmosis of 56.0 kg/cm²G, the sucrose isolation velocity of 7.3 kg/hour is achieved. Other reverse osmosis membranes similar to "SU-200", commercially available from companies other than Toray Engineering Kabushiki Kaisha, also gave similar results.

Table 2

Ingredients	Weight (kg)
Sucrose fatty acid ester (stearate)	0.4
Sucrose	39.0
Potassium lactate	9.0
Soap and fatty acid	5.1
Subtotal	53.5
Water	481.0
Total	534.5

Like this, by repeating the reverse osmosis membrane treatment, both the salt derived from the catalyst and the added neutral salt are sufficiently removed from the aqueous solution. The thus obtained aqueous solution containing sucrose can keep a sucrose concentration of about 15 to 20 % by weight. It is economically disadvantageous as well as technical difficulty to obtain the aqueous solution of sucrose with a concentration of more than 20 % by weight by the reverse osmosis means. Accordingly, when it is desired to obtain the aqueous solution of sucrose having a sucrose concentration of more than 20 % by weight, the solution is concentrated by using a usual concentration apparatus such as a multiple effect evaporator to the desired concentration such as not less than 50 % by weight. Thus recovered sucrose can be reused to

the synthesis of SE as a raw material or used for other purposes.

(Washing of the precipitate)

5 The SE precipitated and separated in the salting out step is in the form of a slurry. It still contains a slight amount of impurities such as salts and sucrose. It has been found that these impurities can be easily removed by treating the slurry with an acidic water.

An aqueous slurry or cake of crude SE obtained in the salting out step is washed with an aqueous solution of an acid having a pH of 3.0 to 5.5. The acid is not particularly limited. Preferable examples of the
10 acid are, for instance, a mineral acid such as hydrochloric acid or sulfuric acid, and an organic acid such as acetic acid or lactic acid. Preferably, the acid solution is kept at a temperature of 10° to 40°C. By this treatment, the impurities such as sucrose, neutral salt and catalyst-derived salt can be transferred into the acidic water. When the temperature of the acidic water is higher than 40°C, the viscosity rises, as previously described, to hinder the operation in addition to a fear of acid decomposition of SE if the
15 operation for a long period of time, for example, over several months, is required. On the other hand, it is uneconomical to keep the acidic water at a low temperature lower than 10°C, because a cooling device is required therefor. Accordingly, the acid solution treatment is effected usually at a temperature of 10° to 40°C, preferably at ordinary temperature.

The above-mentioned three components included as impurities in the cake or slurry, namely unreacted,
20 sucrose, neutral salt and salt formed by neutralization of the catalyst, should be removed as much as possible from the cake or slurry by the acid treatment. Accordingly, it is desirable that the SE cake or slurry is in the form of particles as small as possible so that the impurities are easily released or eluted into water upon washing with acidic water. This can be efficiently attained by conducting the washing in a device having an ability to break into small particles, for example, a mixer (such as "homomixer" made by
25 Tokushu Kiki Kogyo Kabushiki Kisha), a homogenizer, or a colloid mill, whereby substantially the whole amounts of the above-mentioned impurities included in the SE cake or slurry can be transferred into the acidic water.

In the washing of the precipitate with an acidic water, there is observed a noticeable phenomenon that SE having a high HLB (hereinafter referred to as "high HLB-SE") included in the precipitate begins to
30 dissolve into the acidic water. The solubility of high HLB-SE varies depending on the temperature, pH, etc. of the system. For example, when the temperature and pH of the system are ordinary temperature and 3.5, respectively, the equilibrium relationship between the distribution of SE having a high HLB in aqueous phase and SE having a low HLB in the cake is as shown in Fig. 1.

The high HLB-SE has a high solubility in water, and here it is referred to as "water-soluble SE" and
35 assigned with mark "Y". Since Y has a high HLB and accordingly a high water solubility, it does not precipitate even in the acidic aqueous solution and is present therein in a dissolved state. In contrast, SE having a low HLB (hereinafter referred to as "low HLB-SE") is low in water solubility, and in general it tends to deposit in an acidic water having a certain acidity. Here, the low HLB-SE is referred to as "deposable SE" and assigned with mark "X". Since X has a low HLB, it is apt to deposit from an acidic aqueous
40 solution thereof.

Fig. 1 shows a part of a triangular graph wherein the total of monoester, diester and triester is 100 %. In Fig. 1, point M indicates the composition of original sample SE, point X indicates the composition of the depositable SE which has a low HLB, and point Y indicates the composition of the water-soluble SE which has a high HLB. Also, suffixes 1, 2 and 3 attached to M, X and Y show SE having a different proportions of
45 sucrose esters (different ester distribution).

For example, in Fig. 1, when an aqueous acid solution of pH 3.5 is added to a SE sample M₂ consisting of 73 % by weight of monoester, 22 % by weight of diester and 5 % by weight of triester so that the concentration of SE is 3 % by weight, the SE is divided into a depositable SE (X₂) consisting of 68 % by weight of the monoester, 25 % by weight of the diester and 7 % by weight of the triester, and the water-soluble SE (Y₂) consisting of 84 % by weight of the monoester, 13 % by weight of the diester and 3 % by
50 weight of the triester.

The weights WX₂ of X₂ and WY₂ of Y₂ divided from M₂ are obtained by solving the following equations (a) and (b):

$$55 \quad WM_2 = WX_2 + WY_2 \quad (a)$$

$$WY_2 \cdot \overline{Y_2 M_2} = WX_2 \cdot \overline{X_2 M_2} \quad (b)$$

wherein $\overline{Y_2M_2}$ is the distance between point M_2 and point Y_2 , $\overline{X_2M_2}$ is the distance between point X_2 and point M_2 , WM_2 is the weight of M_2 , WX_2 is the weight of X_2 , and WY_2 is the weight of Y_2 , provided that the weights are those of the dried matters.

Like this, SE having a relatively high monoester content (namely SE having a high HLB) is easy to dissolve into the acidic water, whereas SE having a relatively low monoester content (namely SE having a low HLB) is easy to present on the precipitate side. By utilizing this property, the SE included in the reaction mixture can be quantitatively divided into a high HLB-SE and a low HLB-SE. There has also been found a tendency that in general, the higher the monoester content in SE, the more increased the amount of SE (Y) dissolved in water be, and in the reverse case, the amount of SE (Y) dissolved in water is decreased.

The solid component remaining after the washing with the aqueous acid solution is then separated and dried. The purity can be further increased by repeating the washing procedure prior to the drying, thus the low HLB-SE having a high purity is obtained.

Since the aqueous acid solution obtained in the washing step contains a relatively large amount of high HLB-SE, it is separated from the solid SE composed mainly of low HLB-SE in a usual manner such as filtration or centrifugation. The obtained filtrate or supernatant contains, in addition to the high HLB-SE, small amounts of salts and sucrose and, therefore, it is necessary to further purify the SE.

By many experiments we have found that ultrafiltration is suitable for removing these impurities from high HLB-SE in the filtrate or supernatant.

(Ultrafiltration)

It seems that sucrose fatty acid ester molecules aggregate with each other to form apparent high molecular weight micelles under certain conditions in the aqueous solution.

Sucrose monoester, diester and triester are compounds wherein 1, 2 or 3 fatty acid residues are attached to any of oxygen atoms of the 3 primary hydroxyl groups of sucrose molecule, respectively. As well known, since the monoester is low in ability to form micelles in water while having a larger hydrophilic property than diester and triester, it forms a relatively low weight micelle (in other words, a micelle having a small diameter). In contrast, the diester and triester have a very large micelle forming ability while being relatively low in hydrophilic property and, therefore, they form micelles of large apparent molecular weight (namely large micellar diameter).

According to the investigation of the present inventors, since high HLB-SE having a high monoester content, for instance, as high as 70 %, forms micelles of a lower apparent molecular weight in comparison to low HLB-SE having a monoester content as low as 50 %, the microscopic diameter of micelle is small as much and it has a tendency to pass through a ultrafiltration membrane having a specified pore diameter in comparison with low HLB-SE having a monoester content of 50 %. Therefore, high HLB-SE having a high monoester content has an undesirable tendency to pass through the membrane together with the unreacted sucrose, a salt formed by neutralization of a reaction catalyst with an acid, and the like. Such a problem can be easily eliminated by selecting the ultrafiltration membrane, and it is necessary for recovery of high HLB-SE to select the membrane having a relatively low fractionation molecular weight (namely small pore diameter) when desired to remove sucrose and the salts from high HLB-SE having a high monoester content, and it is necessary for recovery of low HLB-SE having a low monoester content to select the membrane having a relatively large fractionation molecular weight (namely large pore diameter).

It is confirmed by the present inventors that it is practically impossible to separate from SE the unreacted fatty acid methyl ester, soap and fatty acid included in the reaction mixture by a filtration means because they are present in the state of being included in the micelles of SE. In other words, impurities permeable together with water to a filtration membrane having an appropriate fractionation molecular weight by a given pressure as actuating force are the unreacted sucrose, the salt derived from the catalyst and the neutral salt added, while the unreacted fatty acid ester, soap and free fatty acid are entrapped in the sucrose ester micelles and they are not impermeable to the filtration membrane.

Thus, in this ultrafiltration step, by skillfully utilizing these facts and by selecting a filtration membrane having an appropriate fractionation molecular weight, the unreacted sucrose and the salts are removed together with water from other components, namely SE, unreacted fatty acid ester, soap and fatty acid.

In order to select a ultrafiltration membrane having an adequate fractionating molecular weight, it is necessary to previously known approximate molecular weights of the subject substances. The molecular weights of typical single compounds involved in the present invention are defined approximately as follows:

- (1) Sucrose = 342
- (2) Unreacted fatty acid methyl ester
(main) Methyl stearate = 290

(3) Salt produced by neutralization of catalyst (K_2CO_3)

In case of lactic acid: potassium lactate = 128

In case of acetic acid: potassium acetate = 98

(4) Neutral salt

NaCl = 58.5

(5) Sucrose fatty acid ester (single compound not forming micelle)

(main) Sucrose monostearate = 600

(main) Sucrose distearate = 858

(main) Sucrose tristearate = 1116

Other sucrose fatty acid esters such as myristate, palmitate, arachate and behenate have also similar molecular weights to the above molecular weights.

(6) Soap

(main) Sodium stearate = 298

(main) Potassium stearate = 314

(7) Fatty acid

(main) Stearic acid = 276

(8) Water = 18

On the supposition that the apparent molecular weight of a sucrose fatty acid ester micelle may be approximately estimated as follows, if 10 molecules associate per micelle, the apparent molecular weight of the micelle is:

molecular weight of monoester (600) X 10 = 6,000 (regarded as 100 % monoester),

molecular weight of diester (858) X 10 = 8,580 (regarded as 100 % diester), and

molecular weight of triester (1,116) X 10 = 11,160 (regarded as 100 % triester).

Since the actual SE is a mixture composed mainly of mono-, di- and triesters, the apparent molecular weight of a SE micelle is defined as the average value thereof.

The selection of a membrane for ultrafiltration adequate for the purposes of the present invention is conducted as follows:

In case of a ultrafiltration membrane having a fractionation molecular weight of 200, even if it is attempted to remove the unreacted sucrose and the salts such as K_2CO_3 while feeding the washing liquid obtained in the previous step with applying a pressure, the components separable by such a membrane are only water and the salts which have lower molecular weights than the fractionation molecular weight 200 of the membrane. Since sucrose which has a molecular weight of 342 larger than the fractionation molecular weight 200, is impermeable to the membrane, it cannot be separated and removed from SE.

In case of a ultrafiltration membrane having a fractionating molecular weight of 5,000, sucrose and the salts can easily pass through fine pores of the membrane, since they have a molecular weight less than 5,000. SE forms micelles as mentioned above, and accordingly it is estimated to have an apparent molecular weight of 6,000 or more on the assumption that the number of sucrose ester molecules associated may be 10 or more. Therefore, the micelles would not be permeable to the membrane having a fractionation molecular weight of 5,000. Since the apparent molecular weight of the micelle would be in fact more than 6,000, a membrane having a fractionation molecular weight of more than 5,000 can be used and this is experimentally confirmed by the present inventors.

Investigation has been made also with respect to a membrane having a fractionation molecular weight of 1,000. The results are as expected, and such a membrane can be used in the present invention.

The ultrafiltration membrane is selected from those having a fractionation molecular weight of 1,000 or more in view of the size or weight of micelles of the sucrose fatty acid esters, treatment efficiency and other conditions. According to the present invention, by suitably selecting the fractionation molecular weight of the ultrafiltration membrane, it is possible to efficiently remove impurities including sucrose.

The ultrafiltration membrane should also satisfy the following conditions.

(1) It has a resistance to a physical external force.

(2) It has a thermal resistance, and is not decomposed by microorganisms.

(3) It has an appropriate fractionation molecular weight and has a large treating ability.

(4) The working life is long.

(5) It is available with an economical cost.

The advance of technique of the preparation of ultrafiltration membrane in recent years is marked, and therefore the membranes satisfying the above conditions are available also from those put on the market.

The washing liquid, namely an aqueous solution containing a water-soluble high HLB-SE (Y), obtained in the prior step, is neutralized with an alkali prior to conducting the ultrafiltration to adjust to a pH of 6.2 to 8.2, preferably a pH in the vicinity of 7.5 in order to prevent the hydrolysis of SE. When the pH is more than

8.2, the hydrolysis of SE is easy to occur. When the pH is less than 6.2, micelles of the SE are hard to be formed, thus resulting in loss of SE due to passing through filtration membrane, or resulting in choking of pores of the membrane.

The thus neutralized aqueous solution is kept at a temperature of not higher than 80 °C during the ultrafiltration regardless of the kind of the fatty acid methyl ester. When the temperature of the aqueous solution exceeds 80 °C, SE may begin to be decomposed. In particular, the highest filtration velocity is obtained when the temperature of the aqueous solution to be filtered falls within the range of 40 ° to 60 °C. That is to say, unreacted sucrose, salt derived from the catalyst such as K_2CO_3 and neutral salt added can pass the most efficiently through the filtration membrane with water, when the filtration temperature is kept at 40 ° to 60 °C, especially in the vicinity of 50 °C. The reason is considered that as a result that SE forms huge micelles at a temperature of 40 ° to 60 °C, the total number of micelles decreases and substances which do not take part in micelle formation, such as unreacted sucrose and the salts, become hard to subject to a resistance of SE, thus these substances such as unreacted sucrose and the salts become easy to move and pass through the membrane.

The SE-containing aqueous solution maintained at a temperature of 40 ° to 60 °C is brought into contact with a ultrafiltration membrane at a hydrogen ion concentration corresponding to a pH of 6.2 to 8.2 under a pressure of 1 to 20 kg/cm²G applied as actuation source for ultrafiltration by a pump.

As stated before, it is important to determine the fractionation molecular weight of filtration membrane so that the impurities can be separated efficiently without leakage of SE at a high filtration velocity. The present inventors have found that membranes having a fractionation molecular weight of 1,000 to 100,000 are suitable for the purposes of the present invention, whereby the purification can be carried out without impairing the separability of unreacted sucrose and salts at a high filtration velocity, and particularly membranes having a fractionation molecular weight of about 5,000 is the most suitable for the treatment on an industrial scale. The filtration velocity decreases with decreasing the fractionation molecular weight. On the other hand, when the fractionation molecular weight is high, namely within a range exceeding 5,000 and up to 100,000, the sucrose ester may leak. However, such a leakage is slight even if occurs, and is not economically detrimental.

Cellulose membranes are not much preferred in practical use, since they are weak against a physical force and are easily attacked with microorganisms. Polysulfone and polyvinylidene fluoride membranes reinforced by a support layer are suitable in practical use, and these filtration membranes are commercially available. They have excellent thermal, acid and alkali resistances and can withstand a physical external force, and moreover microorganisms do not propagate on the membrane surface. Representative examples of commercially available ultrafiltration membranes suitable for the process of the present invention are, for instance, polyvinylidene fluoride membrane (trade mark "TERP-E-5") and polysulfone membranes (trade mark "TERP-HF-10" and "TERP-HF-100") which are sold by Toray Engineering Kabushiki Kaisha.

By the ultrafiltration treatment, impurities such as sucrose and salts are removed from the washing liquid obtained in the prior step of washing the precipitate with acidic water, thus a high HLB-SE (Y) having a high purity is recovered usually in the form of a 5 to 15 % by weight aqueous solution. The thus purified SE contains the monoesters in a high proportion. For example, in case of the crude SE (M_2) having a monoester content of 73 % by weight shown in Fig. 1, it is divided into a high HLB-SE having a monoester content of 84 % by weight and a low HLB-SE having a monoester content of 68 % by weight. Such a high HLB-SE has hitherto not been prepared easily on an industrial scale.

(Drying)

The thus obtained aqueous solution of high HLB-SE can be concentrated up to about 25 % by weight in a usual manner under vacuum, but the solution form is inconvenient for handling, transportation or the like. Preferably, the high HLB-SE should be in the form of a powder. Spray drying is optimum for the dehydration of the aqueous SE solution, and has many advantages as compared with other drying methods.

The spray drying is also suitable for the drying of the low HLB-SE obtained in the form of a slurry in the washing step by separating from the washing liquid. The pH of the slurry is adjusted to a neutral region. The thus pH-adjusted slurry is usually composed of SE, the unreacted fatty acid methyl ester, soap and fatty acid and has a solid content of 1 to 50 % by weight.

As mentioned before, in case of using a usual vacuum dryer as represented by a so-called agitated vacuum dryer, or a flash dryer, deterioration of the quality such as rise in acid value of SE product, coloration or caramel formation is unavoidable due to peculiar viscosity characteristic and low softening or melting point of SE, and in the latter case, a risk of dust explosion cannot be disregarded, too. The spray drying according to the present invention can solve these problems.

In the present invention, the aqueous SE solution or the slurry is continuously fed to a spray drying tower by a pump, dispersed in the form of mist through a nozzle or by a centrifugal force of a rotary disk, and brought into contact with a dry air stream. Since the surface area of water evaporation is made extremely large by spray drying, dehydration and drying can be completed in a very short time, e.g. in several seconds after spraying. The rotary disc type dryer is preferred from the viewpoint of a high viscosity of the solution. Preferably, the solid content of the slurry or the concentration of the SE solution is from 4 to 40 % by weight.

The SE solution fed to the spray drying tower is kept at a temperature of 40° to 80° C, preferably 40° to 60° C in consideration of quality. In case of spraying the solution or slurry by means of a rotary disk, the number of rotations thereof is from 15,000 to 24,000 r.p.m. when the diameter of the disk is from 5 to 10 cm.

The air fed to the tower should have a heat energy sufficient to evaporate water in the solution, and accordingly when the temperature of the air is low, a large quantity of air is required as a matter of course. The temperature of the air can be selected from a range of 10° to 100° C, but in consideration of drying efficiency and prevention of thermal decomposition of the sucrose ester product, the temperature of the air is preferably selected from a range of 60° to 80° C.

The humidity of the air fed is also important as well as the temperature, and it is economical that the absolute humidity of the air is from 0.008 to 0.05 kg water/kg dry air, especially from 0.01 to 0.04 kg water/kg dry air.

The parameters such as volume, diameter and height of the spray drying tower are determined on the basis of the above-mentioned spraying conditions. Under appropriate conditions, powder of SE having a water content of not more than 5 % by weight can be continuously taken out from the lower part of the tower. The obtained dry product is very excellent in quality, e.g. color and stench, because of short heat history, and also this drying work does not require many hands.

In general, the thus obtained powder contains 0.5 to 5.0 % by weight of water, 0.5 to 10.0 % by weight of unreacted fatty acid methyl ester, 0.5 to 60.0 % by weight of a soap, 0.5 to 10.0 % by weight of a fatty acid and 98.0 to 15.0 % by weight of high HLB-SE.

Like this, according to the purification technique using water of the present invention, purified SE can be easily obtained without using an organic solvent, while sucrose can be easily recovered in a high purity. Further, washing of the crude SE with an acidic water provides the high HLB-SE in the form of an aqueous solution and the purified low HLB-SE in the form of an aqueous slurry. The aqueous solution of high HLB-SE can be easily purified by ultrafiltration. When the concentrate obtained in the ultrafiltration is further spray-dried, a dry powder of highly pure high HLB-SE having a good flowability can be easily, continuously obtained without impairing the quality, e.g. color and stench. The slurry of the low HLB-SE can also be spray dried to give a dry powder.

The present invention is more specifically described and explained by means of the following Examples in which all % are by weight unless otherwise noted. It is to be understood that the present invention is not limited to these Examples.

Example 1

A reaction mixture formed by a reaction of sucrose and methyl stearate according to the aqueous medium method was neutralized with lactic acid and was dried. The composition of the dried matter is shown in Table 3.

Table 3

Ingredients	Amount	
	%	kg
SE (stearate)*	40.2	40.2
Unreacted sucrose	32.5	32.5
Unreacted fatty acid methyl ester (methyl stearate)	2.0	2.0
Potassium lactate	1.2	1.2
Soap	23.3	23.3
Stearic acid	0.8	0.8
Total	100.0	100.0

(Note): * SE had a monoester content of 65 % and a di- or higher-ester content of 35 %

To 100 kg of the dried matter was added 2,000 kg of water to dissolve it.

To the obtained aqueous solution was added 100 kg of NaCl and the temperature was elevated to 80 °C. The resulting precipitate was filtered off to give a slurry (solid content: 45.0 %). The amount of the filtrate was 1,950 kg.

To the slurry was added 2,000 kg of aqueous hydrochloric acid solution (pH 3.5) having room temperature, whereby a white precipitate was immediately formed. The resulting aqueous dispersion (pH 3.8) was thoroughly stirred in a homomixer to wash and uniformly break the precipitate into small particles, and was then filtered. An aqueous solution of acetic acid (pH 3.8) was added to the obtained precipitate and washed. This washing operation was repeated two times in total. The precipitate filtered off was adjusted to pH 7.5 with sodium hydroxide. The pH-adjusted precipitate slurry had a solid content of 32 %, and the dried matter thereof had the composition shown in Table 4.

Table 4

Ingredients	Amount	
	%	kg
SE	58.1	34.0
Unreacted fatty acid methyl ester	3.0	1.8
Soap	37.1	23.0
Fatty acid	7.3	0.8
Sucrose	0.5	0.3
Total	100.0	59.9

The total amount of the filtrate obtained in the washing step was 6,000 kg. The solutes included in the filtrate was as shown in Table 5.

Table 5

Ingredients	Amount	
	%	kg
SE	22.60	4.0
Unreacted sucrose	18.08	3.2
Unreacted fatty acid methyl ester	1.12	0.2
Soap and fatty acid	1.69	0.3
Salts	56.51	10.0
Subtotal	100.0	17.7
Water		5,982.3
Total	100.0	6,000.0

After adjusting 6,000 kg of the filtrate to pH 7.5 with sodium hydroxide, it was fed to a spiral type 4 inch cylindrical pressure filtration unit (4 inch X 1m) with membrane area 80 m² equipped with a ultrafiltration membrane having a fractionation molecular weight of 5,000 (commercially available under the trade mark "TERP-E-5" from Toray Engineering Kabushiki Kaisha) under the following conditions.

Temperature: 49 ° to 50 ° C

Discharge velocity of filtrate: 35 to 45 kg/min.

Circulation velocity inside the membrane: 200 to 220 kg/min.

After about 145 minutes from the start of feeding, to 170 kg of the concentrate which had not passed through the ultrafiltration membrane was added 5,820 kg of water, and it was stirred for dissolution and fed to the above cylindrical pressure filtration unit again under the same conditions. This filtration operation was repeated four times in total. The obtained concentrate had a composition (as the dried matter) shown in Table 6 and a solid content of 10.1 %.

Table 6

Ingredients	Amount	
	%	kg
SE	88.8	4.0
Unreacted fatty acid methyl ester	4.5	0.2
Soap and fatty acid	6.7	0.3
Salts	0.0	0.0
Sucrose and others	0.0	0.0
Total	100.0	4.5

The concentrate having the composition shown in Table 6 was heated in a vacuum to concentrate to a solid concentration of 24 %, and spray dried under the following conditions.

Diameter of spray drying tower: 2.0 m

Length of true cylindrical portion: 1.5 m

Fed air: 350 N m³/hour

Diameter of rotary disk: 10 cm

Number of rotations of the disk: 24,000 r.p.m.

Temperature of air at inlet: 70 ° C

Absolute humidity of air at inlet: 0.020 kg water/kg dry air

Feeding velocity of concentrate: 1.3 kg/hour

The powdery high HLB-SE obtained from the lower part of the spray drying tower had a water content of 1.9 %, a bulk specific gravity of 0.42, no coloration due to heating and a good flowability. The drying was continued stably. The composition of the obtained powder is shown in Table 7.

Table 7

Ingredients	Amount (%)
SE*	88.7
Unreacted fatty acid methyl ester	4.4
Soap and fatty acid	6.9
Salts	0.0
Sucrose and others	0.0
Total	100.0

(Note) * SE had a monoester content of 79.0 % and a di- or higher-ester content of 21.0 %.

As shown above, from the SE having the monoester content of 65.0 % (di- or higher-ester content: 35 %) in the original reaction mixture, the high HLB-SE having the monoester content of 79.0 % could be obtained.

The SE left as the solid in washing of the slurry with acidic water was a low HLB-SE having the composition shown in Table 4. The slurry was kept at 60 °C and spray dried in the same manner as above under the following conditions.

Diameter of spray drying tower: 2.0 m

Length of true cylindrical portion: 1.5 m

Fed air: 350 N m³/hour

Diameter of rotary disk: 10 cm

Number of rotations of the disk: 21,000 r.p.m.

Temperature of air at inlet: 55 °C

Absolute humidity of air at inlet: 0.020 kg water/kg dry air

Feed velocity of slurry: 1.1 kg/hour

The powdery low HLB-SE obtained from the lower part of the spray drying tower had a water content of 2.1 %, a bulk specific gravity of 0.46, no coloration due to overheating and had a good flowability. The drying was continued stably, and no trouble such as sticking of the powder to the inner wall surface of the drying tower was observed. Also, there was no change in the monoester content 61 % between before and after the drying.

Next, 1,000 kg of water was added to 1,950 kg of the filtrate (aqueous solution containing sucrose and salts, obtained by removing high HLB-SE precipitated by the previous treatment) to give 2,950 kg of an aqueous solution. The aqueous solution (pH 7.3) was then heated at a temperature of 50 ° to 52.5 °C, and was fed to a reverse osmosis membrane "SU-200" (Toray's trade mark) having a diameter of 4 inches, a length of 1 m and a filtrating area of 80 m² at a pump pressure of 60.0 kg/cm²G under the following operation conditions.

Discharge velocity of the aqueous solution passed through the reverse osmosis membrane: 40 to 33 l/minute

Circulation velocity inside the membrane: 200 to 300 l/minute

Feeding time: about 80 minutes

The concentrate which had not passed through the membrane contained sucrose, and the filtrate which had passed through the membrane, had the compositions shown in Table 8. Thus, sugar was recovered.

Table 8

Ingredients	Filtrate		Concentrate	
	kg	%	kg	%
SE	0.0	0.0	2.2	5.5
Unreacted sucrose	0.1	0.1	28.9	71.7
Soap and fatty acid	0.0	0.0	0.0	0.0
Salts	82.0	99.9	9.2	22.8
Subtotal	82.1	100.0	40.3	100.0
Water	2467.9		359.7	
Total	2550.0		400.0	

Example 2

To 400 kg of the concentrate (solute concentration: 10.0 %) having the composition shown in Table 6, obtained in Example 1 was added 1,600 kg of water, and the thus obtained aqueous solution was fed to the reverse osmosis membrane under the same conditions as in Example 1 to isolate sucrose.

The results are shown in Table 9.

Table 9

Ingredients	Filtrate		Concentrate	
	kg	%	kg	%
SE	0.0	0.0	2.2	6.85
Unreacted sucrose	0.3	3.7	28.6	89.1
Soap and fatty acid	0.0	0.0	0.0	0.0
Salts	7.9	96.3	1.3	4.05
Subtotal	8.2	100.0	32.1	100.00
Water	1699.8		259.9	
Total	1708.0		292.0	

Example 3

To 292 kg of the concentrate (solute concentration: 11.0 %) shown in Table 9, obtained in Example 2 was added 1,708 kg of water and the thus obtained aqueous solution was fed into the reverse osmosis membrane under the same conditions as in Example 1 to isolate sucrose. The results are shown in Table 10.

Table 10

Ingredients	Filtrate		Concentrate	
	kg	%	kg	%
SE	0.0	0.0	2.2	7.1
Unreacted sucrose	0.0	0.0	28.6	92.3
Soap and fatty acid	0.0	0.0	0.0	0.0
Salts	1.11	100.0	0.19	0.6
Subtotal	1.11	100.0	31.0	100.0
Water	1719		249.0	
Total	1720		280.0	

Example 4

The same aqueous slurry as in Table 4 having a solid content of 32 % as obtained in the acid washing step of Example 1 was spray dried in the same manner as in Example 1 except that the slurry was kept at 55 ° C and fed at a velocity of 0.8 kg/hour and the temperature of air at the inlet was kept at 60 ° C.

The obtained low HLB-SE powder had a water content of 1.8 %, a bulk specific gravity of 0.41, a good flowability and no coloration due to overheating. There was no change in the monoester content and acid value of SE. Also, sticking of the powder to the wall of the drying tower was not observed.

In addition to the ingredients used in the Examples, other ingredients can be used in the Examples as set forth in the specification to obtain substantially the same results.

Claims

1. A process for preparing a powder of sucrose fatty acid esters, which comprises
 - a. reacting sucrose with a fatty acid alkyl ester in an aqueous reaction system containing a catalyst to produce a sucrose fatty acid ester,
 - b. adjusting the resulting reaction mixture to a neutral pH region,
 - c. adding water and a neutral salt to the reaction mixture to precipitate the sucrose fatty acid ester product containing sucrose fatty acid and esters having high and low HLB,
 - d. separating the resulting precipitate from the liquid phase,
 - e. extracting the high HLB fraction by washing the precipitate with an acidic water,
 - f. subjecting the resulting washing liquid to ultrafiltration,
 - g. spray drying the resulting concentrate in the form of an aqueous solution, and
 - h. recovering the unreacted sucrose by subjecting the liquid phase of step d) to reverse osmosis.
2. The process of Claim 1, wherein said reaction mixture to be treated consists essentially of 15 to 74 % by weight of sucrose fatty acid esters, 1.0 to 80 % by weight of unreacted sucrose, 0.5 to 10 % by weight of unreacted fatty acid methyl ester, 0.05 to 7.0 % by weight of a catalyst, 1.0 to 60 % by weight of a soap, and 0.5 to 10 % by weight of a fatty acid.
3. The process of Claim 1, wherein said neutral region is from pH 6.2 to pH 8.2.
4. The process of Claim 1, wherein after the addition of water and neutral salt, the reaction mixture is heated to a temperature of 50 ° to 80 ° C.
5. The process of Claim 1, wherein said water is added to the reaction mixture in a water/reaction mixture ratio of 5 : 1 to 40 : 1 by weight.
6. The process of Claim 1, wherein the pH adjustment of the reaction mixture is made with an acid selected from the group consisting of lactic acid, acetic acid, hydrochloric acid and sulfuric acid.

7. The process of Claim 1, wherein the fatty acid radical mainly included in each of the fatty acid alkyl ester, soap and fatty acid is a saturated fatty acid radical having 16 to 22 carbon atoms common to them.
- 5 8. The process of Claim 1, wherein said neutral salt to be added to the reaction mixture is a salt selected from the group consisting of sodium chloride, Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O}$), potassium lactate and potassium acetate.
- 10 9. The process of Claim 1, wherein said sucrose fatty acid ester is composed of 10 to 75 % by weight of the monoester and 90 to 25 % by weight of the di- and higher esters.
11. The process of Claim 1, wherein said acidic water has a pH of 3.0 to 5.5.
- 15 11. The process of Claim 1, wherein said acidic water is maintained at a temperature of 10° to 40° C.
12. The process of Claim 1, wherein the membrane used for the ultrafiltration is made of a polysulfone or a polyvinylidene fluoride.
- 20 13. The process of Claim 1, wherein the membrane for the ultrafiltration has a fractionation molecular weight of 1,000 to 100,000.
14. The process of Claim 1, wherein said ultrafiltration is carried out under a pressure of 1.0 to 20.0 kg/cm²G.
- 25 15. The process of Claim 1, wherein the washing liquid is neutralized to pH 6.2 to 8.2.
16. The process of Claim 1, wherein the washing liquid subjected to ultrafiltration is maintained at a temperature of 40° to 60° C.
- 30 17. The process of Claim 1, wherein a membrane used for the reverse osmosis has a fractionation molecular weight of 150 to 200.
18. The process of Claim 1, wherein said liquid phase is maintained at a temperature of 40° to 60° C and at a pH of 6.2 to 8.2.
- 35 19. The process of Claim 1, wherein said liquid phase has a source content of 10 to 20 % by weight.
20. The process of Claim 1, wherein said concentrate to be spray-dried has a solid content of 4 to 40 % by weight.
- 40 21. The process of Claim 1, wherein said spray drying is conducted in an air stream having an absolute humidity of 0.008 to 0.05 kg water/kg dry air and a temperature of 10° to 100° C.
22. The process of Claim 1, wherein the precipitate washed with an acidic water is spray-dried.
- 45 23. The process of Claim 22, wherein the precipitate to be spray-dried is in the form of an aqueous slurry having a solid content of 4 to 40 % by weight.

Patentansprüche

- 50 1. Verfahren zur Herstellung eines Pulvers von Sucrosefettsäureestern, welches umfaßt:
 - a. Reagieren von Sucrose mit einem Fettsäurealkylester in einem wässrigen Reaktionssystem, das einen Katalysator enthält, um einen Sucrosefettsäureester herzustellen,
 - b. Einstellen der resultierenden Reaktionsmischung auf einen neutralen pH-Bereich,
 - 55 c. Zugeben von Wasser und einem neutralen Salz zur Reaktionsmischung, um das Sucrosefettsäureester-Produkt auszufällen, das Sucrosefettsäure und -ester mit hohem und niedrigem HLB enthält,
 - d. Abtrennen des resultierenden Niederschlags von der flüssigen Phase,
 - e. Extrahieren der hohen HLB-Fraktion durch Waschen des Niederschlags mit saurem Wasser,

- f. Unterwerfen der resultierenden Waschflüssigkeit der Ultrafiltration,
- g. Sprühtrocknen des resultierenden Konzentrats in Form einer wässrigen Lösung und
- h. Zurückgewinnen der nichtumgesetzten Sucrose durch Unterwerfen der flüssigen Phase von Schritt d) der Umkehrosmose.

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2. Verfahren nach Anspruch 1, worin die zu behandelnde genannte Reaktionsmischung im wesentlichen besteht aus: 15,0 bis 74,0 Gewichtsprozent Sucrosefettsäureestern, 1,0 bis 80,0 Gewichtsprozent nichtumgesetzte Sucrose, 0,5 bis 10,0 Gewichtsprozent nichtumgesetzter Fettsäuremethylester, 0,05 bis 7,0 Gewichtsprozent eines Katalysators, 1,0 bis 10,0 Gewichtsprozent einer Seife, 0,5 bis 10,0 Gewichtsprozent einer Fettsäure.

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3. Verfahren nach Anspruch 1, worin der genannte neutrale Bereich von pH 6,2 bis pH 8,2 ist.

4. Verfahren nach Anspruch 1, worin nach der Zugabe des Wassers und des neutralen Salzes, die Reaktionsmischung auf eine Temperatur von 50 °C bis 80 °C erhitzt wird.

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5. Verfahren nach Anspruch 1, worin genanntes Wasser zur Reaktionsmischung in einem Wasser/Reaktionsmischung-Verhältnis von 5:1 bis 40:1, bezogen auf das Gewicht, hinzugegeben wird.

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6. Verfahren nach Anspruch 1, worin die pH-Einstellung der Reaktionsmischung mit einer Säure durchgeführt wird, die aus der Gruppe ausgewählt ist, die aus Milchsäure, Essigsäure, Salzsäure und Schwefelsäure besteht.

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7. Verfahren nach Anspruch 1, worin das Fettsäureradikal, das in jedem von Fettsäurealkylester, Seife und Fettsäure hauptsächlich enthalten ist, ein gesättigtes Fettsäureradikal mit 16 bis 22 Kohlenstoffatomen ist, das ihnen gemeinsam ist.

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8. Verfahren nach Anspruch 1, worin genanntes, der Reaktionsmischung hinzuzusetzendes neutrale Salz ein Salz ist, das aus der Gruppe ausgewählt ist, die aus Natriumchlorid, Glaubersalz ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), Kaliumlactat und Kaliumacetat besteht.

9. Verfahren nach Anspruch 1, worin genannter Sucrosefettsäureester aus 10 bis 75 Gewichtsprozent Monoester und aus 90 bis 25 Gewichtsprozent Di- und höheren Estern zusammengesetzt ist.

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10. Verfahren nach Anspruch 1, worin genanntes saures Wasser einen pH von 3,0 bis 5,5 hat.

11. Verfahren nach Anspruch 1, worin genanntes saures Wasser auf einer Temperatur von 10 °C bis 40 °C gehalten wird.

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12. Verfahren nach Anspruch 1, worin die zur Ultrafiltration verwendete Membran aus Polysulfon oder Polyvinylidenfluorid hergestellt ist.

13. Verfahren nach Anspruch 1, worin die genannte Membran für die Ultrafiltration ein Trennungsmolekulargewicht von 1000 bis 100000 aufweist.

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14. Verfahren nach Anspruch 1, worin die genannte Ultrafiltration unter einem Druck von 1,0 bis 20,0 kg/cm²G durchgeführt wird

15. Verfahren nach Anspruch 1, worin die Waschflüssigkeit auf pH 6,2 bis 8,2 neutralisiert wird.

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16. Verfahren nach Anspruch 1, worin die der Ultrafiltration unterworfenen Waschflüssigkeit auf einer Temperatur von 40 ° bis 60 °C gehalten wird.

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17. Verfahren nach Anspruch 1, worin eine für die Umkehrosmose verwendete Membran ein Trennungsmolekulargewicht von 150 bis 200 aufweist.

18. Verfahren nach Anspruch 1, worin die genannte flüssige Phase bei einer Temperatur von 40 °C bis 60 °C und einem pH von 6,2 bis 8,2 gehalten wird.

19. Verfahren nach Anspruch 1, worin die genannte flüssige Phase einen Sucrose-Gehalt von 10 bis 20 Gewichtsprozent aufweist.

20. Verfahren nach Anspruch 1, worin das genannte sprühzutrocknende Konzentrat einen Festgehalt von 4 bis 40 Gewichtsprozent aufweist.

21. Verfahren nach Anspruch 1, worin das genannte Sprühtrocknen in einem Luftstrom mit einer absoluten Feuchte von 0,008 bis 0,05 kg Wasser/kg Trockenluft und einer Temperatur von 10 bis 100 °C durchgeführt wird.

22. Verfahren nach Anspruch 1, worin der mit einem sauren Wasser gewaschene Niederschlag sprühgetrocknet wird.

23. Verfahren nach Anspruch 22, worin der genannte sprühzutrocknende Niederschlag in Form einer wässrigen Aufschlämmung mit einem Festgehalt von 4 bis 40 Gewichtsprozent vorliegt.

Revendications

1. Un procédé de préparation d'esters de saccharose gras sous forme de poudre, qui comprend

- la réaction de saccharose à un alkyl ester gras dans un système de réaction aqueux contenant un catalyseur pour produire un ester de saccharose gras,
- l'ajustement du mélange de réaction résultant à une zone de pH neutre,
- l'addition d'eau et d'un sel neutre au mélange de réaction pour précipiter le produit d'ester de saccharose gras contenant de l'acide gras de saccharose et des esters à fort et à faible HLB,
- la séparation du précipité résultant de la phase liquide,
- l'extraction de la fraction à fort HLB par lavage du précipité avec une eau acide,
- la soumission du liquide de lavage résultant à l'ultrafiltration,
- le séchage par atomisation du concentré résultant sous forme d'une solution aqueuse, et
- la précipitation du saccharose non réagi en soumettant la phase liquide de l'étape d) à une osmose inverse.

2. Le procédé selon la revendication 1, dans lequel ledit mélange de réaction à traiter se compose essentiellement de 15 à 74 % en masse d'esters de saccharose gras, 1,0 à 80 % en masse de saccharose non réagi, 0,5 à 10 % en masse d'ester de méthyle gras non réagi, 0,05 à 10 % en masse d'un acide gras.

3. Le procédé selon la revendication 1, dans lequel ladite zone neutre présente un pH se situant entre 6,2 et 8,2.

4. Le procédé selon la revendication 1, dans lequel On a chauffé le mélange de réaction à une température allant de 50 à 80 ° C, après l'addition d'eau et de sel neutre.

5. Le procédé selon la revendication 1, dans lequel on ajoute ladite eau au mélange de réaction selon un rapport eau/mélange de réaction de 5:1 à 40:1 en masse.

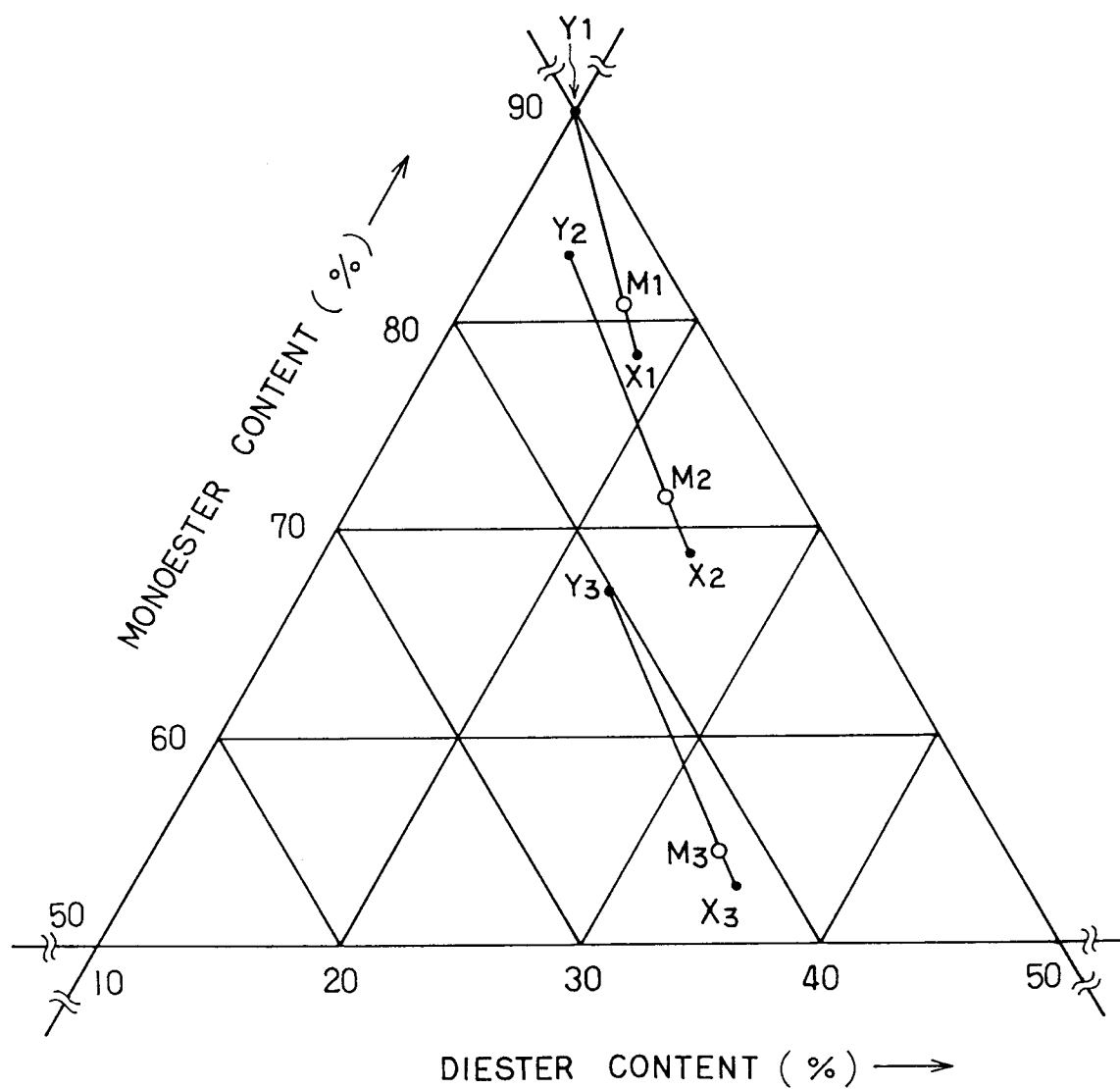
6. Le procédé selon la revendication 1, dans lequel l'ajustement du pH du mélange de réaction est réalisé avec un acide sélectionné parmi le groupe comprenant de l'acide lactique, de l'acide acétique, de l'acide chlorhydrique et de l'acide sulfurique.

7. Le procédé selon la revendication 1, dans lequel le radical d'acide gras contenu en majorité dans l'alkyl ester gras, le savon et l'acide gras est un radical d'acide gras saturé contenant 16 à 22 atomes de carbone en communs avec eux.

8. Le procédé selon la revendication 1, dans lequel ledit sel neutre à ajouter au mélange de réaction est un sel sélectionné parmi le groupe comprenant du chlorure de sodium, du sel de Glauber ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), du lactate de potassium et de l'acétate de potassium.

9. Le procédé selon la revendication 1, dans lequel ledit ester de saccharose gras est composé de 10 à 75 % en masse du monoester et 90 à 25 % en masse des diester et ester supérieur.
10. Le procédé selon la revendication 1, dans lequel ladite eau acide présente un pH situé entre 3,0 et 5,5.
11. Le procédé selon la revendication 1, dans lequel ladite eau acide est maintenue à une température allant de 10 à 40 ° C.
12. Le procédé selon la revendication 1, dans lequel la membrane utilisée pour l'ultrafiltration est composée d'un fluorure de polyvinylidène et de polysulfone.
13. Le procédé selon la revendication 1, dans lequel la membrane pour l'ultrafiltration présente un poids moléculaire de fractionnement situé entre 1000 et 100 000.
14. Le procédé selon la revendication 1, dans lequel ladite ultrafiltration est réalisée sous une pression allant de 1,0 à 20,0 kg/cm² G.
15. Le procédé selon la revendication 1, dans lequel le liquide de lavage est neutralisé à un pH situé entre 6,2 et 8,2.
16. Le procédé selon la revendication 1, dans lequel le liquide de lavage soumis à l'ultrafiltration est maintenu à une température allant de 40 à 60 ° C.
17. Le procédé selon la revendication 1, dans lequel une membrane utilisée pour l'osmose inverse présente un poids moléculaire de fractionnement situé entre 150 et 200.
18. Le procédé selon la revendication 1, dans lequel ladite phase liquide est maintenue à une température située entre 40 et 60 ° C, et à un pH allant de 6,2 à 8,2.
19. Le procédé selon la revendication 1, dans lequel ladite phase liquide présente une teneur en saccharose située entre 10 et 20 % en masse.
20. Le procédé selon la revendication 1, dans lequel ledit concentré à sécher par atomisation présente une teneur en solide allant de 4 à 40 % en masse.
21. Le procédé selon la revendication 1, dans lequel ledit séchage par atomisation est réalisé dans un courant d'air présentant une humidité absolue située entre 0,008 et 0,05 kg eau/kg air sec et une température allant de 10 à 100 ° C.
22. Le procédé selon la revendication 1, dans lequel le précipité lavé à une eau acide est séché par atomisation.
23. Le procédé selon la revendication 1, dans lequel le précipité à sécher par atomisation se présente sous forme d'une boue aqueuse ayant une teneur en solide allant de 4 à 40 % en masse.

FIG. 1



$$\text{MONOESTER} + \text{DIESTER} + \text{TRIESTER} = 100\%$$